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TECHNICAL MEMORANDUM

U.S. NAVAL APPLIED SCIENCE LABORATORY
NAVAL BASE
BROOKLYN I, NEW YORK

USNASL-9110-P-1J

REPORT OF INVESTIGATIONS

on

SYNTHESIS AND THERMAL RESISTANCE OF POLYMERS CONTAINING Si-O AND Zr-O BONDS

SR 007-03-03, Task 1000

Lab. Project 6135, Technical Memorandum 1

29 JUL 1963

PHYSICAL SCIENCES DIVISION

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Associate Technical Director

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Ref: (a) NAVSHIPYDNYK ltr 974:ltb, A11, Lab. Project 6135, Progress Report 1 of 12 Jun 1959
(b) NAVSHIPYDNYK ltr 974:eew, Lab. Project 6135, Progress Report 4 of 5 Dec 1960
(c) NAVSHIPYDNYK ltr 974:im, Lab. Project 6135 of 11 Mar 1963
(d) MATLAB NAVSHIPYDNYK, Lab. Project 6135, Progress Report 7 of 30 Jul 1962
(e) MATLAB NAVSHIPYDNYK, Lab. Project 6135, Progress Reprot 8 of 27 Feb 1963
(f) MATLAB NAVSHIPYDNYK, Lab. Project 6135, Progress Report 6 of May 1962
(g) Visit of MATLAB Personnel (Code 9420 - B. Simms and A. Delman) to BUSHIPS (Code 342A - E. Bukzin) of 13 Jun 1963

1. This Laboratory is conducting a continuing program to develop techniques for the synthesis of novel semi-inorganic macromolecular products for use by the Navy in applications requiring polymeric materials having high resistance to pyrolytic attack.

2. These studies are being made under the supervision of B. B. Simms, Naval Applied Science Laboratory, Organic Chemistry Branch Head (Code 9420); E. A. Bukzin, Bureau of Ships, Program Manager (Code 342A, OX-66748); and W. B. Shetterly, Bureau of Ships, Project Engineer (Code 634C4, OX-63309).

3. The results of previous studies in this program have been summarized in references (a), (b) and (c). This work included studies involving the synthesis of substances containing Si-O and Zr-O linkages, which was presented originally in reference (d). In general, this phase of these investigations indicated the feasibility of synthesizing such copolymers by condensation reactions of diphenylsilanediol and tetrabutoxyzircane. These macromolecular products which are comprised chiefly of cyclic structures, are less thermally stable than are the linear silbiphenylene and perphenylated siloxane polymers discussed previously in references (e) and (f), respectively. Reference (d) also provided information regarding the synthesis and thermal properties of polymeric phenoxy- and butoxyzircane oxides. As expected, the phenoxy-product proved to be more heat stable than the butoxy-substance, probably because of the stabilizing influence of the benzene ring.

4. In continuation, experiments were designed to prepare new intermediate products for use in the synthesis of novel copolymers containing main-chains of Si-O and Zr-O linkages with phenyl and phenoxy pendant groups, respectively. These studies resulted in the preparation of specimens 1A and 1B described in Table 1. Thermogravimetric analyses indicate that the material containing 55.6% Zr is more thermally resistant than the product having 43.2% Zr.

5. Table 1 also describes and gives the thermal properties of copolymers 2, 3A & 3B which were obtained by reaction of diphenylsilanediol with the intermediate substances described above. On the basis of the thermogravimetric analyses data, it is suggested that the heat stabilities of the copolymers are substantially the same as that of the intermediate zirconium products 1A & 1B from which they were prepared. Data are also given in Table 1 for three macromolecular substances which were synthesized by reaction of diphenylsilanediol with diphenoxyzircane-diacetylactenonate, which was previously reported in reference (d) as exhibiting a 50% loss of volatilizable components

at 360°C, when heated in air at 180°C/hr. The thermogravimetric analyses data shows these copolymers, designated as specimens 4A, 4B, and 4C, attain the same volatilization point when heated similarly to 360, 370, and 355°C, respectively. This indicates, as in the case of specimens 2, 3A, and 3B, that the inherent heat resistance of the intermediate product is the limiting factor for the thermal stabilities exhibited by the copolymers.

6. The copolymers reported herein and those described previously in reference (d) are not as pyrolytically stable as the silbiphenylene and perphenylated siloxane polymers discussed in references (e) and (f), respectively. In addition, these materials exhibit poor hydrolytic stability, due probably to the vulnerability to attack by water of the butoxy and phenoxy groups. Therefore, further syntheses efforts along these lines are being discontinued. Instead, studies are now underway along the following lines:

a. Compounds such as $(C_6H_5)_3GeOH$, $(C_6H_5)_2AsOH$, $(C_6H_5)_2BOH$, and $(C_6H_5)_3SnOH$ are being prepared or purchased for use as intermediates in the synthesis of new copolymers containing silicon-oxygen and metal-oxygen linkages, through the Lewis Acid catalyst procedure described in reference (f).

b. Studies are being made to broaden the range of applicability of the silarylene polymers described in reference (f), by enhancing their engineering properties through selective modifications of their molecular structures. For example, efforts are now underway to synthesize silarylene substance with phenyl and vinyl pendant groups. The vinyl groups should provide the active sites necessary to permit the crosslinking of these products and thereby make these materials more useful as high temperature resistant coatings, potting compounds, dielectrics, etc.

c. Visits to governmental agencies and industrial research activities engaged in high temperature polymer syntheses studies will be continued, but with slightly increased frequency as discussed in reference (g). In addition, the intensive surveillance of the pertinent technical literature will be continued to provide the latest scientific information. Materials whose publicized properties suggest potential suitability for naval end-item applications will be obtained, whenever available, for examination and possible limited structural modification studies by the Laboratory.

A. D. Delman

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Principal Investigator

TABLE 1

PROPERTIES OF ZIRCONIUM-CONTAINING SUBSTANCES

Specimen No.	Reactants	Product Description	Thermal Stability Properties: Temperature at 50% Loss of Volatilizable Components (°C)	% Weight Loss: 300°C	400°C	500°C
1A	$ZrCl_4$ and C_6H_5OH	Dark, reddish-violet, hard, benzene soluble resin, containing 55.6 and 10.6% Zr and Cl, respectively (molar ratio Zr:Cl=2:1).	400	7.4	12.4	24.6
1B	"	Hard, pink, benzene insoluble powder, containing 43.2 and 13.4% Zr and Cl, respectively (molar ratio Zr:Cl=5:4).	220	23.6	26.5	30.0
2	1A Product and $(C_6H_5)_2Si(OH)_2$	Reddish-black, hard, brittle, benzene insoluble resin, containing 46.0, 3.4, and 7.5% Zr, Si, and Cl, respectively (molar ratio Zr:Si:Cl= 4.2:1:1.7).	400	8.4	13.9	25.8
3A	1B Product and $(C_6H_5)_2Si(OH)_2$	Reddish-pink, hard, brittle, benzene soluble resin, containing 27.0, 10.2, and 5.7% Zr, Si, and Cl, respectively (molar ratio Zr:Si:Cl= 2:2.5:1).	240	24.8	28.0	33.8
3B	"	Pink, friable, benzene insoluble powder, containing 43.8, 5.7, and 8.8% Zr, Si, and Cl, respectively (molar ratio Zr:Si:Cl=2.4:1:1.25).	250	15.9	20.8	24.7
4A	Diphenoxyzircane-Diacetylacetonate and $(C_6H_5)_2Si(OH)_2$	Orange, hard, brittle, benzene and ligroin soluble resin, containing 6.2 and 7.5% Zr and Si, respectively (molar ratio Zr:Si=1:4).	360	26.5	43.9	58.0
4B	"	Dark brown, hard, brittle, benzene soluble and ligroin insoluble resin, containing 13.7 and 6.3% Zr and Si, respectively (molar ratio Zr:Si=2:3).	370	15.4	39.7	55.9
4C	"	Dark brown, hard benzene and ligroin insoluble powder, containing 28.1 and 2.8% Zr and Si, respectively (molar ratio Zr:Si=3:1).	355	18.5	38.2	52.8